

Phase Behavior of Carbon Dioxide Mixtures with n-Alkanes and n-Perfluoroalkanes

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Abstract

The phase behavior of mixtures containing carbon dioxide, *n*-alkanes and *n*-perfluoroalkanes is studied using the statistical associating fluid theory for potentials of variable attractive range (SAFT-VR). The molecules are modelled as fully flexible chains of tangentially bonded attractive spherical segments of hard-core diameter \mathbf{s} . The attractive interactions are treated via square-well potentials of depth \mathbf{e} and range \mathbf{l} . The pure component intermolecular parameters for carbon dioxide and the *n*-alkane molecules were determined in previous works by fitting to vapor pressures and saturated liquid densities; the same procedure is followed in this work to determine the parameters for the *n*-perfluoroalkane molecules. The optimized conformal parameters (\mathbf{s} and \mathbf{e}) are rescaled with the experimental critical point of each of the pure components. A set of transferable mixture parameters is presented, which provide a good description of the mixtures phase behavior, and additionally offer an insight into the higher solubility of *n*-perfluoroalkanes in carbon dioxide as compared to the solubility of *n*-alkanes.

Keywords: Equation of state, SAFT, phase equilibria, solubility, carbon dioxide.

Introduction

The development of amphiphilic molecules for use as surfactants in supercritical carbon dioxide (CO₂) and other supercritical fluids has led to the study of micellar and microemulsion phases in supercritical fluid media. Diblock copolymers are often used for this purpose since they can self-assemble into micelles when placed in supercritical carbon dioxide. To date, the most successful surfactants for use in supercritical carbon dioxide have contained perfluorinated chains as the CO₂-philic part [1]. Unfortunately, highly fluorinated compounds are expensive, and thus there is great incentive to design new, inexpensive CO₂-philic groups.

In order to design surfactants with tailored solubility in CO₂, knowledge of the intermolecular amphiphile-solvent interactions is essential. There is still, however, considerable controversy over the origin of the solvation power of CO₂, in particular in relation to the origin of the exceptional solubility of fluorinated polymeric compounds. It is well known that fluorinated compounds are more soluble in CO₂ than their hydrocarbon counterparts [2, 3]. Iezzi *et al.* [2] carried out experimental measurements of the phase behavior of CO₂ + *n*-hexane and CO₂ + *n*-perfluorohexane and showed that the differences in phase behavior between CO₂-*n*-hexane and CO₂-*n*-perfluorohexane are consistent with the differences in pure-component critical parameters. Yee *et al.* [3] found, from dielectric constant measurements, no evidence of any special attractive interactions between CO₂ and perfluoroethane. Moreover, they suggested that CO₂ is more repulsive to perfluoroethane than to ethane on the basis of observed frequency shifts of the ν_2 bending mode of CO₂ in perfluoroethane and ethane, and concluded that the enhanced solubility of perfluorocarbons in CO₂ is due to the highly repulsive nature of fluorocarbon-fluorocarbon interactions, which make the solute-solute interactions less favorable than the solute-solvent interactions. Dardin *et al.* [4] studied the proton and fluorine chemical shifts of *n*-hexane, *n*-perfluorohexane, and 1,1-dihydroperfluorooctylpropionate dissolved in supercritical carbon dioxide using high-pressure, high-resolution nuclear magnetic resonance. They attribute the excess magnetic shielding to van der Waals interactions between the fluorinated sites in the solute and carbon dioxide.

Additionally, various theoretical approaches including *ab initio* calculations have also been applied to this problem. Cece *et al.* [5] credited, from Hartree-Fock calculations, the enhanced binding in the CO₂-C₂F₆ to the electrostatic interaction between the positively charged carbon atom of CO₂ and the negatively charged fluorine atoms in the fluorocarbon. These findings agree with the experimental results of Dardin *et al.* [4]. However, Diep *et al.* [6], in contrast to the study by Cece *et al.* [5], do not find any enhanced attraction between CO₂ and perfluorocarbons relative to the analogous hydrocarbons, and concluded that it is not possible to discern the reason for the greater solubility of perfluorocarbons than of hydrocarbons in CO₂ from calculations on the small clusters used in their study. Cui *et al.* [7] have also studied the vapor-liquid behavior of *n*-alkane and carbon dioxide + *n*-perfluoro-*n*-alkane and carbon dioxide binary mixtures using the Gibbs ensemble Monte Carlo simulation technique. They employed molecular simulation with simple interaction-

site models to explore the effects of van der Waals interactions between *n*-hexane and CO₂ and between *n*-perfluorohexane and CO₂. Their results suggest that the dispersion interaction and the geometric packing may have a predominant role in accounting for the solubility difference between *n*-alkane and *n*-perfluoroalkane in CO₂. Thus, a complete theory of the mixing of perfluoroalkanes with CO₂ is still lacking at the moment, and a satisfactory interpretation for this enhanced solubility has not been established yet. This understanding would be greatly facilitated if it were possible to simulate different process scenarios, with accurate and molecular based equation of state.

In this work we use the statistical associating fluid theory for potentials of variable range (SAFT-VR) [8,9] to study the phase behavior of CO₂ + *n*-alkane and CO₂ + *n*-perfluoroalkane mixtures. The SAFT approach is based on the thermodynamic perturbation theory of Wertheim for associating [10, 11, 12, 13] and chain molecules [14, 15, 16, 17]. It takes into account explicitly repulsive (spherical and chain-like), dispersion, and association (hydrogen bonding) interactions. The work undertaken over the past decade has amply demonstrated that the SAFT framework provides a state-of-the-art thermodynamic description of complex multicomponent mixtures (several recent review articles collect the many applications and modifications of the approach [18, 19, 20, 21]). In the SAFT-VR approach a non-conformal intermolecular potential parameter describes the range of the segment-segment interactions, and the approach can be used to model successfully the phase behavior of mixtures containing small strongly associating and polar molecules such as water [22] and hydrofluorinated refrigerants [23], as well as long-chain molecules such as alkanes [24] and polyethylene [25]. In addition to this, the SAFT-VR EOS has recently been used to study the global phase behavior of CO₂ + *n*-alkane binary mixtures [26, 27]. One of the goals of this previous work was provide model parameters that could be used in a transferable way, and, as we shall see later on, we continue in the same spirit and use the same pure component and mixture parameters in our present work. The phase behavior of binary mixtures of *n*-alkanes (from methane to *n*-heptane) and *n*-perfluoroalkanes (from perfluoromethane to *n*-perfluorobutane) has also been studied previously using transferable parameters [28]. In this work we consider the application of transferable parameters to predict the phase behavior of mixtures containing CO₂, *n*-alkanes (C₆H₁₄, C₇H₁₆, C₈H₁₈) or *n*-perfluoroalkanes (C₆F₁₄, C₇F₁₆), as well as attempting to provide a link between the effective intermolecular parameters of the equation of state, and the differences in phase behavior (in solubility) between *n*-alkanes and *n*-perfluoroalkanes in CO₂.

Models and theory

In the SAFT-VR approach [8,9] the molecules are modeled as chains of tangentially bonded hard spherical segments of diameter s . The attractive interactions are described by square-well potentials of variable range l_{ij} and depth ϵ_{ij} , and the contribution to the free energy due to the dispersion interactions is obtained following the framework of the perturbation theory of Barker and Henderson [30, 31, 32]. As in other SAFT approaches, association interactions can also be considered through embedded short-range attractive interaction sites, but in this work we treat non-associating molecules, and so this

contribution is not necessary. The Helmholtz free energy A for an n -component mixture of CO_2 , n -alkane and n -perfluoroalkane molecules can thus be written as,

$$\frac{A}{NkT} = \frac{A^{\text{IDEAL}}}{NkT} + \frac{A^{\text{MONO}}}{NkT} + \frac{A^{\text{CHAIN}}}{NkT}, \quad (1)$$

where N is the number of molecules, k the Boltzmann constant, and T the temperature. The ideal gas contribution to the free energy is given by a sum over all species i in the mixture [29]

$$\frac{A^{\text{IDEAL}}}{NKT} = \sum_{i=1}^n x_i \ln(\mathbf{r}_i \Lambda_i^3) - 1, \quad (2)$$

where $x_i = N_i/N$ is the mole fraction, $\mathbf{r}_i = N_i/V$ the number density, N_i the number of molecules, V the volume of the system, and Λ_i the thermal de Broglie wavelength of species i . The monomer Helmholtz free energy can be written in terms of the free energy per monomer a^{M} as

$$\frac{A^{\text{MONO}}}{NKT} = \left(\sum_{i=1} x_i m_i \right) a^{\text{M}}, \quad (3)$$

where m_i is the number of spherical segments of chain i . Using the Barker and Henderson [30, 31, 32] perturbation theory for mixtures with a hard-sphere reference system, the monomer free energy per segment can be obtained from the expansion

$$a^{\text{M}} = a^{\text{HS}} + \frac{1}{kT} a_1 + \left(\frac{1}{kT} \right)^2 a_2. \quad (4)$$

The expression of Boublik [33] and Mansoori *et al.* [34] for a multicomponent mixture of hard spheres is used for the reference hard-sphere term,

$$a^{\text{HS}} = \frac{6}{p\mathbf{r}_s} \left[\left(\frac{\mathbf{z}_2^3}{\mathbf{z}_3^2} - \mathbf{z}_0 \right) \ln(1 - \mathbf{z}_3) + \frac{3\mathbf{z}_1\mathbf{z}_2}{(1 - \mathbf{z}_3)} + \frac{\mathbf{z}_2^3}{\mathbf{z}_3(1 - \mathbf{z}_3)^2} \right], \quad (5)$$

where $\mathbf{r}_s = N_s/V$ is the total number density of spherical segments and \mathbf{z}_i are reduced densities. The mean attractive energy a_1 , is obtained from the sum of the partial terms corresponding to each type of pair interaction

$$a_1 = \sum_{i=1}^n \sum_{j=1}^n x_{s,i} x_{s,j} a_{ij}, \quad (6)$$

where, using the mean value theorem, and the van der Waals (vdW) one-fluid approximation (see [8, 9] for more details) each of the monomer-monomer free energy contributions can be written as

$$a_1^{ij} = -\mathbf{r}_s \mathbf{a}_{ij}^{\text{vdw}} g_0^{\text{HS}}(\mathbf{s}_c; \mathbf{z}_c^{\text{eff}}). \quad (7)$$

In the case of a square-well potential the van der Waals attractive constant $\mathbf{a}_{ij}^{\text{vdw}}$ is given by

$$\mathbf{a}_{ij}^{\text{vdw}} = \frac{2}{3} \mathbf{p} \mathbf{e}_{ij} \mathbf{s}_{ij}^3 (\mathbf{I}_{ij}^3 - 1), \quad (8)$$

and $g_0^{\text{HS}}(\mathbf{s}_x; \mathbf{z}_x^{\text{eff}})$ is the contact radial distribution function of a hypothetical pure fluid of average diameter \mathbf{s}_x , and is obtained from the Carnahan and Starling equation of state [35]. The effective packing fraction $\mathbf{z}_x^{\text{eff}}$ is obtained from the corresponding packing fraction of the fluid \mathbf{z}_x using,

$$\mathbf{z}_x^{\text{eff}}(\mathbf{z}_x, \mathbf{I}_{ij}) = c_1(\mathbf{I}_{ij}) \mathbf{z}_x + c_2(\mathbf{I}_{ij}) \mathbf{z}_x^2 + c_3(\mathbf{I}_{ij}) \mathbf{z}_x^3 \quad (9)$$

Coefficients c_1 , c_2 , and c_3 are given in reference [8]. It should be noted that this corresponds to the MX1b mixing rule of reference [9].

The first fluctuation term a_2 is written in terms of a_1 within the local compressibility approximation [8, 9] as

$$a_2 = \sum_{i=1}^n \sum_{j=1}^n x_{s,i} x_{s,j} \frac{1}{2} \mathbf{e}_{ij} K^{\text{HS}} \mathbf{r}_s \frac{\partial a_1^{ij}}{\partial \mathbf{r}_s}, \quad (10)$$

where K^{HS} is the hard-sphere isothermal compressibility of Percus-Yevick [36].

The contribution to the free energy due to chain formation is expressed in terms of the contact value of the monomer background correlation function, y_{ii}^{MONO} as

$$\frac{A^{\text{CHAIN}}}{NkT} = - \sum_{i=1}^n x_i (m_i - 1) \ln y_{ii}^{\text{MONO}}(\mathbf{s}_{ii}) \quad (11)$$

where, for square-well chains $y_{ii}^{\text{MONO}}(\mathbf{s}_{ii}) = y_{ii}^{\text{SW}}(\mathbf{s}_{ii})$, and $y_{ii}^{\text{SW}}(\mathbf{s}_{ii}) = g_{ii}^{\text{SW}}(\mathbf{s}_{ii}) \exp(\mathbf{e}_{ii}/kT)$ [8, 9]. In the SAFT-VR approach the radial distribution function of the system of unbonded monomers is obtained from a high-temperature expansion

$$g_{ii}^{\text{SW}}(\mathbf{s}_{ii}) = g_{ii}^{\text{HS}}(\mathbf{s}_{ii}) + \frac{\mathbf{e}_{ii}}{kT} g_1(\mathbf{s}_{ii}), \quad (12)$$

where the reference term is evaluated using the expression of Boublík [33], and $g_1(\mathbf{s}_{ii})$ from a self-consistent method for the pressure P from the Clausius virial theorem and from the density derivative of the Helmholtz free energy (see reference [8] for more details). Once

the free energy is known, standard thermodynamic relations can be used to determine the pressure and chemical potentials, and the phase equilibria conditions (equality of temperature, pressure and chemical potentials of each component in all phases) are solved using a numerical algorithm [37].

Results and discussion

Following previous work [26, 27] carbon dioxide is modelled as a non-associating and non-spherical molecule. The attractive dispersion interactions and the quadrupole are treated in an effective way via a square-well potential of depth e_{11} and adjustable range l_{11} . The linear non-spherical nature of the molecule is treated in an explicit way modeling the molecule with 2 tangentially bonded square-well segments; i.e., $m_1=2$. The values of the parameters were obtained in previous work by fitting to experimental vapor pressures and saturated densities; the resulting values are presented in table 1 here for completeness.

The n -alkane molecules have also been studied in a number of previous works with the SAFT-VR approach [24, 26, 27, 28]. The molecules are modeled as chains of m_2 tangentially bonded segments of hard-sphere diameter s_{22} , interacting through square-well potentials of depth e_{22} and range l_{22} . The number of segments m_2 forming the model chain can be obtained as a function of the number of carbon atoms C of the n -alkane molecule by $m_2 = (C-1)/3+1$ [24]. Using this value for m_2 McCabe and Jackson [24] have carried out the optimization of the monomer intermolecular parameters for a large number of n -alkanes (from methane to n -hexatriacontane) using experimental vapor pressures and saturated liquid densities, and have provided linear relationships for each of the parameters as functions of molecular weight. We use the optimized intermolecular parameters in this work, although we rescale the conformal parameters s_{22} and e_{22} to provide an accurate description of the critical point of each of the pure n -alkanes (see [24] and table 1).

Table 1. Optimized SAFT-VR square-well intermolecular potential parameters. The subscript c indicates that the parameters have been rescaled to the experimental critical point. Parameters in *italic* were obtained in this work.

	m	$s / \text{\AA}$	$e / k \text{ (K)}$	l	T_c^*	$p_c^* 10^3$	$s_c / \text{\AA}$	$e_c / k \text{ (K)}$
CO ₂	2.0	2.7864	179.27	1.5257	0.18146	5.1528	3.1364	168.89
C ₆ H ₁₄	2.667	3.920	250.4	1.552	0.1957	3.995	4.479	236.6
C ₇ H ₁₆	3	3.933	251.3	1.563	0.2021	3.607	4.529	237.3
C ₈ H ₁₈	3.333	3.945	250.3	1.574	0.2076	3.275	4.564	236.5
<i>C₆F₁₄</i>	2.85	<i>4.529</i>	<i>277.33</i>	<i>1.4390</i>	<i>0.21448</i>	<i>4.3652</i>	<i>5.0315</i>	<i>264.24</i>
<i>C₇F₁₆</i>	3.22	<i>4.464</i>	<i>285.34</i>	<i>1.4365</i>	<i>0.22179</i>	<i>3.9102</i>	<i>5.1233</i>	<i>272.63</i>

The number of segments m_3 forming a model perfluoroalkane chain is related to the number of carbons of the n -perfluoroalkane molecule by $m_3 = (C-1)*0.37+1$ as in previous works [24]. Using these values for m_3 , parameters for perfluoromethane to n -perfluorobutane have been presented previously [28], but are not available for longer molecules. In the case of n -perfluorohexane a large amount of pure component experimental data is available [38, 39,

40, 41]. Although more limited, some experimental data are also available in the literature for *n*-perfluoroheptane [39, 42, 43, 44]. Hence, we follow the same procedure as in previous works and determine the parameters by comparison to experimental vapor pressures and saturated liquid densities. The optimized intermolecular parameters for the *n*-perfluoroalkane molecules used in this work are presented in table 1.

Once the intermolecular pure component parameters are determined, the calculation of mixture phase behavior requires determining a number of unlike intermolecular parameters. In the case of the SAFT-VR approach for non-associating chain molecules these are: \mathbf{s}_{ij} , \mathbf{e}_{ij} and \mathbf{l}_{ij} . Traditionally, the modified Lorentz-Berthelot combining rules are used [45],

$$\mathbf{s}_{ij} = \frac{\mathbf{s}_{ii} + \mathbf{s}_{jj}}{2}, \quad \mathbf{e}_{ij} = (1 - \mathbf{x}_{ij})\sqrt{\mathbf{e}_{ij}\mathbf{e}_{ij}}, \quad \text{and} \quad \mathbf{l}_{ij} = (1 - \mathbf{g}_{ij}) \frac{\mathbf{l}_{ii}\mathbf{s}_{ii} + \mathbf{l}_{jj}\mathbf{s}_{jj}}{\mathbf{s}_{ii} + \mathbf{s}_{jj}}. \quad (14)$$

In the case of hard core potentials \mathbf{s}_{ij} is given exactly by the expression shown in equation (14), but the parameters describing the unlike square-well energy \mathbf{e}_{ij} and range \mathbf{l}_{ij} are only approximate, so that two adjustable parameters \mathbf{x}_{ij} and \mathbf{g}_{ij} often need to be introduced in order to improve the agreement with the experimental mixture phase behavior. The adjustable parameters used in this work are presented in table 2.

Table 2. SAFT-VR square-well intermolecular potential parameters for the binary mixtures.

<i>System</i>	ξ_{12}	γ_{12}
CO ₂ + C ₆ H ₁₄	0.88	0.989
CO ₂ + C ₆ F ₁₄	0.88	0.989
C ₆ F ₁₄ + C ₇ F ₁₆	0.923	1

Values of $\xi_{12} = 0.88$ and $\gamma_{12} = 0.989$ were determined in previous works [26, 27] to ensure that the mixture of CO₂ (1) + *n*-C₁₃H₂₈ (2) exhibits type IV phase behavior in the classification of Scott and van Konynenburg [46], and it was shown that the parameters can be transferred to study the global phase behavior, and the transitions between types of phase diagram of a large number of mixtures of the CO₂ (1) + *n*-alkane (2) homologous series. Here we show that the same parameters provide a good description of the vapor-liquid equilibria in CO₂ + *n*-hexane mixtures (see figure 1), at constant temperatures of 40 °C and 80 °C, in good agreement with experimental data [2, 47, 48]. It can be seen in this figure that the slope of the liquid composition at the lowest temperature (the closest to the critical point of CO₂) is somewhat different than suggested by the experimental data: considering that the calculations are totally predictive, we still find the results very encouraging. Moreover, the set of parameters used is not temperature dependent, so that it can be used to describe the phase behavior of the mixture for the entire fluid range, and can be transferred to other CO₂ (1) + *n*-alkane (2) mixtures [26, 27].

In the case of the mixture of CO₂ (1) + *n*-perfluorohexane (3) we find the same unlike adjustable intermolecular parameters can be used; i.e., $\xi_{13} = 0.88$, and $\gamma_{13} = 0.989$. A

comparison of the SAFT-VR calculations using these parameters with experimental data [2] is presented in figure 2. The choice of parameters may, at first, seem surprising (perfluoroalkane molecules are known to be more soluble in CO_2 than alkane molecules). In our SAFT-VR model we have treated the quadrupolar interactions characteristic of carbon dioxide in an effective way through square-well potentials, and the parameters ξ_{ij} and γ_{ij}

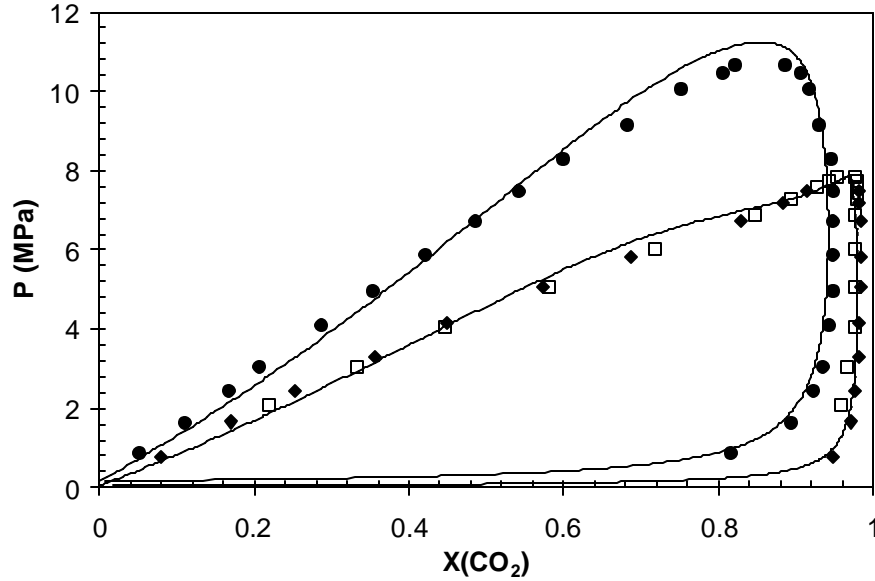


Figure 1. Vapor-liquid equilibrium for the $\text{CO}_2(1) + n\text{-hexane}(2)$ binary mixture compared with the SAFT-VR predictions. Symbols represent the experimental data at: (●) 353 K [47], (□) 313 K [48] and (◆) 313 K [47]. The theoretical predictions are shown by the continuous curves.

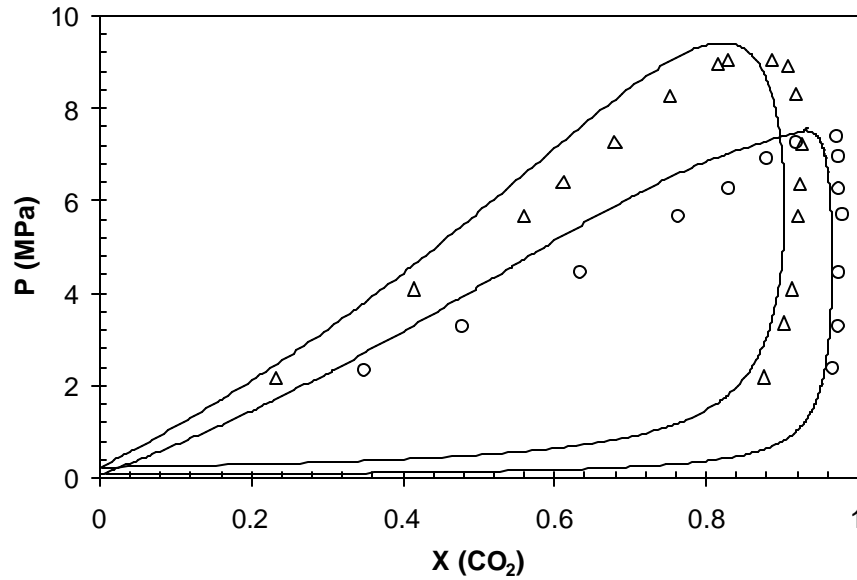


Figure 2. Vapor-liquid equilibrium for the $\text{CO}_2(1) + n\text{-perfluorohexane}(3)$ binary mixture compared with the SAFT-VR predictions. Symbols represent the experimental data at: (Δ) 353 K and (○) 313 K [2]. The theoretical predictions are shown by the continuous curves.

mainly provide a correction of this approximation. In this view, it makes sense to obtain similar correction parameters for both mixtures studied. To support this idea we refer to the work of Cui *et al.* [7], who have obtained the phase behavior of a mixture of CO₂ + *n*-hexane and of CO₂ + *n*-perfluorohexane using computer simulations. In their work charge-charge interactions are incorporated to model carbon dioxide, and they find that the usual Lorentz-Berthelot combining rule can be used to determine the depth in the Lennard–Jones potential both between CO₂ and the *n*-alkane and between CO₂ and the *n*-perfluoroalkane; i.e., the same combining rule can be used for both systems. In our approach it is more useful to compare the unlike van der Waals integrated energy parameters as a measure of the amount of dispersion interaction between components. Using the unlike transferable parameters proposed it is straightforward to calculate the values of a_{ij}^{vdW} from the optimized pure component parameters. The results for the molecules considered are shown in figure 3. From this figure it can be inferred that: a) a *n*-perfluoroalkane will be more soluble in carbon dioxide compare with its corresponding *n*-alkane, as can be observed, e.g. comparing figures 1 and 2; b) the difference in solubilities among *n*-alkanes and *n*-perfluoroalkanes in carbon dioxide decreases when the molecular weight increases, and this is reflected in the differences between the van der Waals integrated energy parameters, which also decreases.

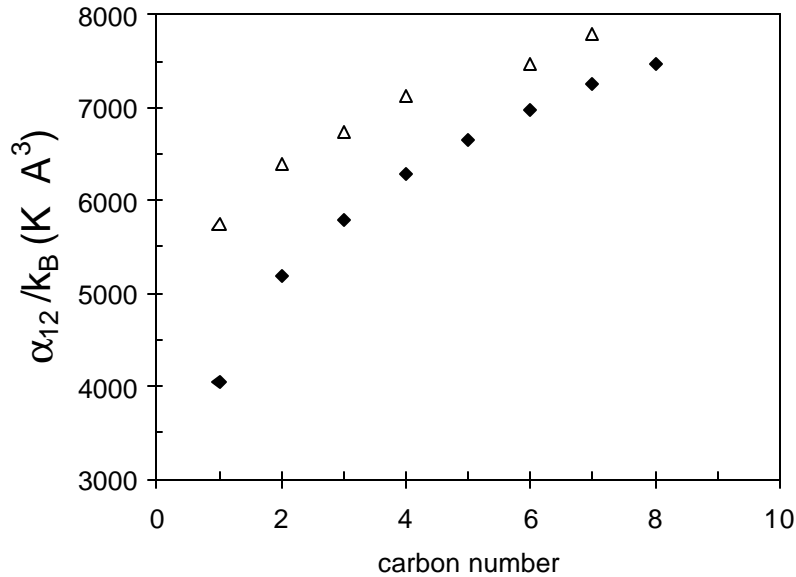


Figure 3. Unlike van der Waals integrated energy parameter, α_{ij}/k_B , as a function of the carbon number for *n*-alkanes (♦) and *n*-perfluoroalkanes (Δ).

Taking advantage of the transferability of parameters, the vapor-liquid phase equilibria for a mixture of CO₂ (1) + *n*-heptane (2), and for a mixture of CO₂ (1) + *n*-perfluoroheptane (2) have been predicted at 37.5 °C. The comparison with experimental data available [49] for the mixture CO₂ (1) + *n*-heptane (2) is presented in figure 4, where the agreement is excellent. No experimental data was found for the system CO₂ (1) + *n*-perfluoroheptane (2). The predictions indicate that *n*-heptane and *n*-perfluoroheptane present similar solubilities

in CO_2 , at least at the conditions studied in figure 4. This result can seem surprising, because low molecular weight n -perfluorohexanes are known to be more soluble than the equivalent n -alkanes in carbon dioxide. However, at present neither experimental nor molecular simulation data are available to corroborate our predictions for the $\text{CO}_2 + \text{C}_7\text{F}_{16}$ system. We note here that in the next section, the phase equilibria of binary n -alkane + n -perfluoroalkane mixtures (including C_7F_{16}) are predicted using the same parameters, and very good agreement is found with the experimental data available.

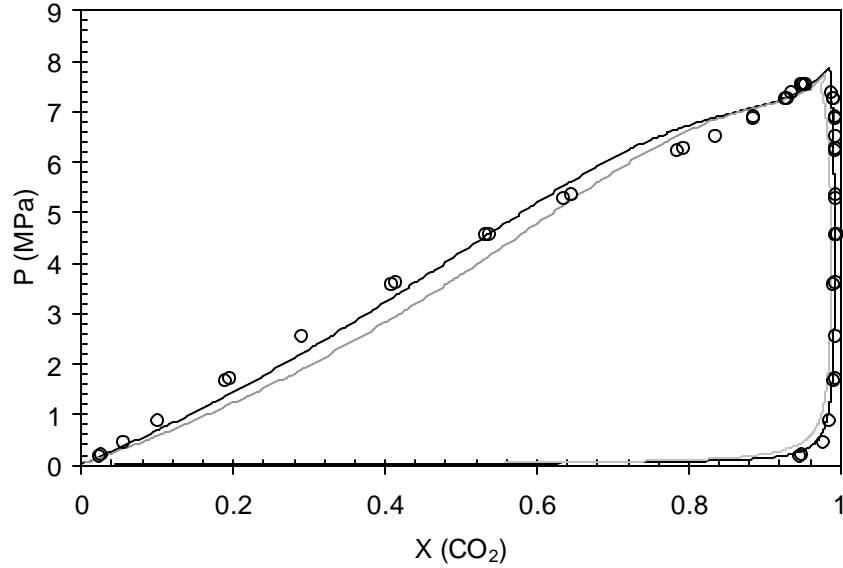


Figure 4 Vapor-liquid equilibrium for the $\text{CO}_2(1) + n$ -heptane (2), and $\text{CO}_2(1) + n$ -perfluoroheptane (3) binary mixtures compared with the SAFT-VR predictions. Symbols represent the experimental data at 310.65 K for $\text{CO}_2(1) + n$ -heptane (2). The theoretical predictions are shown by the continuous curves. Black line: $\text{CO}_2(1) + n$ -heptane, grey line: $\text{CO}_2(1) + n$ -perfluoroheptane (3).

In order to be able to study the phase behavior of ternary mixtures containing CO_2 , n -alkanes, and n -perfluoroalkanes, the alkane-perfluoroalkane unlike intermolecular parameters must also be determined. Binary n -alkane (2) + n -perfluoroalkane (3) mixtures are known to exhibit type II phase behavior in the classification of Scott and van Konynenburg [46] (characterized by the presence of liquid-liquid phase separation and continuous vapor-liquid critical curves) when the difference in chain length between the two components is not very large (symmetric or close-to symmetric systems). Mixtures of the components considered in this work exhibit this type of phase diagram. McCabe *et al.* [28] studied the high-pressure phase behavior of a number of n -perfluoroalkanes (C_1 - C_4) and n -alkane (C_1 - C_7) systems, and suggested a value $\xi_{23} = 0.923$ (with $\gamma_{23} = 0$, as could be expected since both molecules are non-polar). However, in the previous work [28] little liquid-liquid coexistence data were used to determine the unlike ξ_{23} parameter. We find that the slightly different value of $\xi_{23} = 0.929$ (with $\gamma_{23} = 0$) provides a better fit to the upper critical solution temperature (UCST) of $\text{C}_6\text{H}_{14} + \text{C}_6\text{F}_{14}$ [50] (see figure 5a). We note that SAFT is a mean field theory, and so cannot describe the critical region correctly. As in previous cases, the unlike intermolecular parameters can be used in a transferable way; in

figure 5b) the liquid-liquid envelope for a mixture of *n*-heptane (2) + *n*-perfluorohexane (3) is also shown. Note that, as could be expected, the choice of parameters to provide the best agreement of the critical point of the mixture is in detriment of the prediction of the compositions of the liquid phases. We have also calculated the vapor-liquid phase behavior of the *n*-hexane (2) + *n*-perfluorohexane (3) and compared our results with the available experimental data [51] (see figure 6). The mixture presents azeotropic behavior, which is well described by the theoretical approach with the set of transferable parameters chosen for this family of systems, although a small over prediction in the equilibrium pressure is seen as compared to the experimental data. Finally, in figure 7a are shown the predictions for the mole fractions of the liquid and vapor phases for the system *n*-hexane (2) + *n*-perfluoroheptane (3). Excellent agreement is found with the available experimental data [52]. In figure 7b the Pxy behavior of the system $C_6H_{14} + C_6F_{14}$ is compared with the one of $C_6H_{14} + C_7F_{16}$. Even though the azeotropic point is the only experimental data available for the system $C_6H_{14} + C_7F_{16}$, the predictions from the present work are in good agreement.

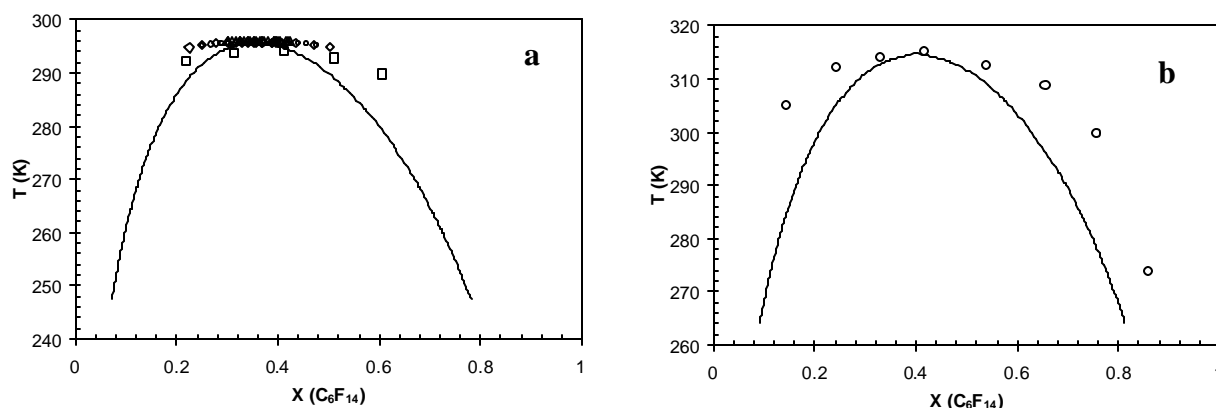


Figure 5. Liquid-liquid equilibrium for (a) the *n*-hexane (2) + *n*-perfluorohexane (3) and (b) *n*-hexane (2) + *n*-perfluoroheptane (3) binary mixtures compared with the SAFT-VR predictions. Symbols represent the experimental data for: $C_6H_{14} + C_6F_{14}$ (●) [51], and $C_6H_{14} + C_7F_{16}$ (Δ) [53], (◊) [54], (□) [51]. The theoretical predictions are shown by the continuous curves.

Our proposed framework supports the proposition that the increased solubility of perfluoroalkanes in CO_2 may be closely related to larger attractive dispersion interactions. Cui et al. [7] have already suggested that packing and dispersion interaction play a major role. In addition to this, the SAFT-VR approach has the advantage of being entirely predictive, so that the phase behavior of a large number of binary mixtures can be studied by fitting only the pure component parameters of the *n*-perfluoroalkane molecules. In future it would be desirable to obtain a parametrization similar to that available for *n*-alkane molecules [24], so that the method could be used in the context of mixture design. The nature of the SAFT approach, and indeed, of most equations of state, is such that only binary interaction parameters are required, so that once the adjustable parameters for a set of binary mixtures are known, multicomponent phase behavior can be easily studied. In future we plan to assess the validity of the predictions in the context of ternary phase behavior.

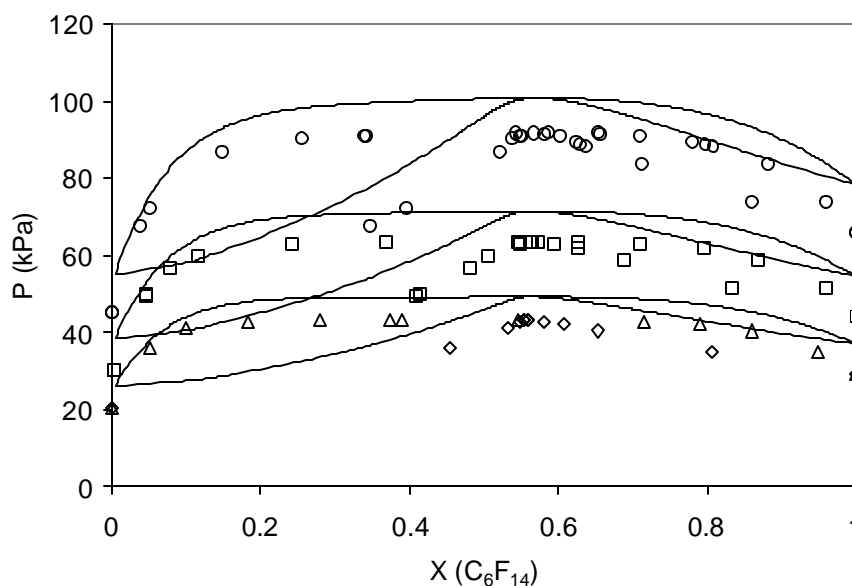


Figure 6. Vapor-liquid equilibrium for the *n*-hexane (2) + *n*-perfluorohexane (3) binary mixture compared with the SAFT-VR predictions. Symbols represent the experimental data of Dunlap et al. [51]: (O) 318 K, (\square) 308 K and (Δ) 298 K. The theoretical predictions are shown by the continuous curves.

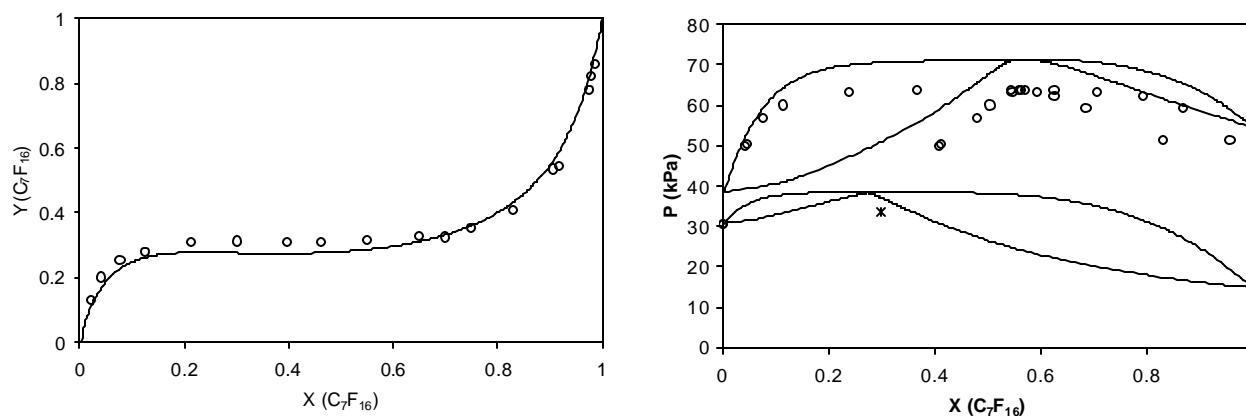


Figure 7. (a) Vapor phase mole fraction vs. liquid phase mole fraction for *n*-hexane (2) + *n*-perfluoroheptane (3) at 308 K. Symbols represent the experimental data of Duce et al. [52]. The theoretical predictions are shown by the continuous curves. (b) Vapor-liquid equilibrium for the *n*-hexane (2) + *n*-perfluoroheptane (3) and *n*-hexane (2) + *n*-perfluoroheptane (3) binary mixtures compared with the SAFT-VR predictions. Symbols represent the experimental data of Duce et al. [52]: (O) for $C_6H_{14} + C_6F_{14}$ and (*) for $C_6H_{14} + C_7F_{16}$. The theoretical predictions are shown by the continuous curves.

Conclusions

The phase behavior of a number of carbon dioxide (CO_2), *n*-alkane (C_6H_{14} , C_7H_{16} , C_8H_{18}) and *n*-perfluoroalkane (C_6F_{14} , C_7F_{16}) binary mixtures has been studied using the statistical associating fluid theory for potentials of variable attractive range (SAFT-VR). The molecules are modelled as chains of tangentially bonded attractive spherical segments, with

the attractive interactions treated as square-well potentials of variable range. Even though the characteristic quadrupole of carbon dioxide is not taken into account explicitly, the approach can be used to predict the phase behavior of the homologous series studied. In future we plan to assess the validity of the predictions in the context of ternary phase behavior. A predictive approach such as the one proposed could be helpful in identifying possible new CO₂-philic groups as well as co-solvents for supercritical CO₂.

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List of Symbols

a_1	mean attractive energy
a_2	first fluctuation term
a^M	free energy per monomer
A	Helmholtz free energy
c_i	coefficients of equation (9)
g_0^{HS}	contact radial distribution function
k	Boltzmann constant
K^{HS}	hard-sphere isothermal compressibility of Percus-Yevick
m_i	number of spherical segments of chain i
N, N_i	number of molecules
V	volume of the system
x_i	mole fraction
T	temperature

Greek symbols

a_{ij}^{vdw}	van der Waals attractive constant
e_{ij}	square-well potentials of depth
z_i	reduced densities
z_x^{eff}	effective packing fraction
z_x	packing fraction of the fluid
r_{ij}	number density
r_s	total number density of spherical segments
l_{ij}	square-well potentials of variable range
L_i	thermal de Broglie wavelength of species i
s	segments of diameter
s_x	average diameter

References

- [1] Buhler, E., Dobrynin, A. V., DeSimone, J. M. and M. Rubinstein, *Macromolecules*, 31 (1998) 7347-7355.
- [2] Iezzi, A., Bendale, P., Enick, R., Turberg, M. and J. Brandy, *Fluid Phase Equilib.* 52 (1989) 307-317.
- [3] Yee, G. G., Fulton, J. L. and R. D. Smith, *J. Phys. Chem.* 96 (1992) 6172-6181.
- [4] Dardin, A., DeSimone, J. M. and E. T. Samulski, *J. Phys. Chem. B*, 102 (1998) 1775 - 1780.
- [5] Cece, A., Jureller, S. H., Kerschner, J. L. and K. F. Moschner, *J. Phys. Chem.* 100 (1996) 7435-7439.
- [6] Diep, P., Jordan, K. D., Johnson, J. K. and E. J. Beckman, *J. Phys. Chem. A*, 102 (1998) 2231 - 2236.
- [7] Cui, S. T., Cochran, H. D. and P. T. Cummings, *J. Phys. Chem. B* 103 (1999) 4485-4491.
- [8] Gil-Villegas, A., Galindo, A., Whitehead, P. J., Mills, S. L., Jackson, G. and A. N. Burgess, *J. Chem. Phys.* 106 (1997) 4168-4186.
- [9] Galindo, A., Davies, L.A., Gil-Villegas, A. and G. Jackson, *Molec. Phys.* 93 (1998) 241-252.
- [10] Wertheim, M. S., *J. Stat. Phys.* 35 (1984) 19-34.
- [11] Wertheim, M. S., *J. Stat. Phys.* 35 (1984) 35-47.
- [12] Wertheim, M. S., *J. Stat. Phys.* 42 (1986) 459-476.
- [13] Wertheim, M. S., *J. Stat. Phys.* 42 (1986) 477-492.
- [14] Jackson, G., Chapman, W. G. and K. E. Gubbins, *Mol. Phys.* 65 (1988) 1 – 31.
- [15] Chapman, W. G., Jackson, G. and K. E. Gubbins, *Mol. Phys.* 65 (1988) 1057 – 1079.
- [16] Wertheim, M. S., *J. Chem. Phys.* 85 (1986) 2929-2936.
- [17] Wertheim, M. S., *J. Chem. Phys.* 87 (1987) 7323-7331.
- [18] Müller, E. A. and K.E. Gubbins, in J.V.Sengers, R.F. Kayser, C.J. Peters and H. J. White, Jr. (Eds), *Equations of State for Fluids and Fluid Mixtures. Experimental Thermodynamics*, Volume 5, Elsevier, Amsterdam, 2000, pp 435-478.
- [19] Müller, E. A. and K. E. Gubbins, *Ind. Eng. Chem. Res.* 40 (2001) 2193-2211.
- [20] Wei, Y.S. and R. Sadus, *AIChE J.*, 46 (2000) 169 –196.
- [21] Economou, I. G. *Ind. Eng. Chem. Res.* 41 (2002) 953- 962.
- [22] Galindo, A., Gil-Villegas, A., Jackson, G. and A.N. Burgess. *J. Phys. Chem. B* 103 (1999) 10272-10281.
- [23] Galindo, A., Gil-Villegas, A., Whitehead, P. J., Jackson, G. and A.N. Burgess. *J. Phys. Chem. B* 102 (1998) 7632-7639.
- [24] McCabe, C. and G. Jackson. *Phys. Chem. Chem. Phys.* 1 (1999) 2057-2064.
- [25] McCabe, C., Galindo, A., Garcia-Lisbona, M. N. and G. Jackson. *Ind. Eng. Chem. Res.* 40 (2001) 3835-3842.
- [26] Blas, F. J. and A. Galindo, *Fluid Phase Equilib.* 194-197 (2002) 501-509.
- [27] Galindo, A. and F. J. Blas, *J. Phys. Chem. B.*, 106 (2002) 4503-4515.
- [28] McCabe, C., Galindo, A., Gil-Villegas, A. and G. Jackson, *J. Phys. Chem. B* 102 (1998) 8060-8069.

-
- [29] J. S. Rowlinson and F. L. Swinton, *Liquids and Liquid Mixtures*, 3rd ed., Butterworth Scientific: London 1982.
- [30] Barker, J. A. and D. J. Henderson, *J. Chem. Phys.* 47 (1967) 2856- 2861.
- [31] Barker, J. A. and D. J. Henderson, *J. Chem. Phys.* 47 (1967) 4714- 4721.
- [32] Barker, J. A. and D. J. Henderson, *Rev. Mod. Phys.* 48 (1976) 587-671.
- [33] Boublik, T., *J. Chem. Phys.* 53 (1970) 471-472.
- [34] Mansoori, G. A., Carnahan, N. F., Starling, K. E. and T. W. Leland, *J. Chem. Phys.* 54 (1971) 1523-1525.
- [35] Carnahan, N. F. and K. E. Starling, *J. Chem. Phys.* 51 (1969) 635-636.
- [36] Percus, J. K. and G. J. Yevick, *Phys Rev.* 110 (1958) 1-13.
- [37] Press, W. H., Teukolsky, S.A., Vetterling, W.T. and B. P. Flannery, *Numerical Recipes in Fortran*, 1st ed., Cambridge University Press: Cambridge, U. K. 1986.
- [38] Crowder, G.A., Taylor, Z. L., Reed, T. M. and J. A. Young, *J. Chem. Eng. Data*, 12 (1967) 481-485.
- [39] Ermakov, H. V. and V. P. Skripov, *Teplofiziki*, 1 (1971) 44-49.
- [40] Dunlap, R. D., Murphy, C. J. Jr. and R. G. Bedford, *J. Am. Chem. Soc.*, 80 (1958) 83-85.
- [41] Mousa, A. H. N., *J. Chem. Eng. Data*, 23 (1978) 133-134.
- [42] Oliver, G. D. and J. W. Grisard, *J. Am. Chem. Soc.*, 73 (1951) 1688-1690.
- [43] Milton, H. T. and G. D. Oliver, *J. Am. Chem. Soc.*, 74 (1952) 3951-3952.
- [44] Oliver, G. D., Blumkin, S. and C. W. Cunningham, *J. Am. Chem. Soc.*, 73 (1951) 5722-5725.
- [45] J.M. Prausnitz, R.N. Lichtenthaler and E. Gomez de Azevedo. *Molecular Thermodynamics of Fluid-Phase Equilibria*. Third Edition. Prentice Hall, New Jersey, 1999.
- [46] Scott, R. L. and P. H. van Konynenburg, *Discuss. Faraday Soc.* 49 (1970) 87-97.
- [47] Li, Y-H., Dillard, K. H. and R.L. Robinson, Jr., *J. Chem. Eng. Data* 26 (1981) 53-55.
- [48] Wagner, Z. and I. Witcherle, *Fluid Phase Equilib.* 33 (1987) 109-123.
- [49] Kalra, H., Kubota, H., Robinson, D. B. and H.J Ng, *J. Chem. Eng. Data*, 23 (1978) 317-321.
- [50] Hicks, C. P. and C. L. Young, *Chem. Rev.* 75 (1975) 119-175.
- [51] Dunlap, R. D., Bedford, R. G., Woodbrey, J. C. and S. D. Furrow, *J. Am. Chem. Soc.*, 81 (1959) 2927-2930.
- [52] Duce, C., Tine, M. R., Lepori, L. and E. Matteoli, *Fluid Phase Equilib.* 199(1-2) (2002) 197-212.
- [53] Block, T. E., Judd, N. F., McLure, I. A., Knobler, C. M. and R. L. Scott, *J. Phys. Chem.*, 85 (1981) 3282-3290.
- [54] Gaw, W. J. and R. L. Scott, *J. Chem. Thermod.* 3 (1971) 335-345.